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(54) Title: FABRIC SOFTENING COMPOSITIONS			
(57) Abstract			
<p>The invention provides a fabric softening composition comprising: i) at least one nonionic fabric softening agent, and ii) at least one anionic surfactant, and iii) at least one cationic polymer wherein the particles formed from i), ii) and iii) have a net negative charge and the composition comprises no more than 1 % by weight of non-polymeric cationic surfactant and/or cationic fabric softening compounds.</p>			

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## FABRIC SOFTENING COMPOSITIONS

### Technical Field

5

The present invention relates to fabric softening compositions, particularly to compositions that soften without adversely affecting the absorbency of the fabric and which deposit well onto the fabric without being

10 detrimentally affected by anionic carry-over from the wash.

### Background and Prior Art

Rinse added fabric softener compositions are well known.

15 However, a disadvantage associated with conventional rinse conditioners is that although they increase the soft feel of a fabric they simultaneously decrease the fabric's absorbency. A decrease in the absorbency properties of a fabric means that its ability to take up water decreases.

20 This is particularly disadvantageous with towels where the consumer requires the towel to be soft, and yet, have a high absorbency.

WO 98/16538 (Unilever) discloses fabric conditioning compositions comprising liquid or soft solid derivatives of a cyclic polyol or a reduced saccharide which give good softening but retain absorbency of the fabric.

EP 0 380 406 (Colgate-Palmolive) discloses detergent compositions comprising a saccharide or reduced saccharide ester containing at least one fatty acid chain.

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WO 95/00614 (Kao Corporation) discloses softening compositions comprising polyhydric alcohol esters and cationised cellulose.

5 DE 19732073 (Henkel) discloses nitrogen free rinse conditioners containing water, anionic surfactants and fatty materials.

US 5 447 643 (Hüls) discloses aqueous fabric softeners 10 comprising nonionic surfactants and mono, di or tri fatty acid esters of certain polyols.

EP 607529 (Huels) discloses nonionic fabric softening agents stabilised by cationic colloids.

15 WO 96/15213 (Henkel) discloses textile softening agents containing alkyl, alkenyl and/or acyl group containing sugar derivatives, which are solid after esterification, in combination with nonionic and cationic emulsifiers.

20 A further problem associated with fabric softening agents that are not cationic in nature is that deposition onto a fabric is often inadequate which generally leads to softening results that are not as good as the consumer 25 requires. In order to achieve deposition of such compositions a cationic surfactant deposition aid is typically used. However such deposition aids are usually adversely affected by anionic carry over from the wash and so high levels are needed to provide good results.

30 The present invention is directed towards alleviating the problems associated with the prior art as referred to hereinabove.

The principal advantages of the present invention include that excellent softening of the fabric is achieved without detriment to the absorbency of the fabric, the softening agent deposits well onto fabric and is not unduly adversely 5 affected by anionic carryover from the wash. Furthermore the compositions are easily manufactured.

Definition of the Invention

10 Thus according to one aspect of the invention there is provided a fabric softening composition comprising:

- (i) at least one nonionic fabric softening agent and
- 15 (ii) at least one anionic surfactant, and
- (iii) at least one cationic polymer

wherein the particles formed from i), ii) and iii) have an 20 overall net negative charge and the composition comprises no more than 1% by weight non-polymeric cationic surfactant and/or cationic fabric softening compounds.

It has been found, surprisingly, that these compositions 25 provide an unexpected combination of simultaneous fabric softening and retention of absorbency and also deposit well onto the fabric without being detrimentally affected by anionic carry-over from the wash.

30 The invention also provides a method of depositing a nonionic fabric softening agent onto fabric from a fabric softening composition, comprising emulsifying the softening

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agent with an anionic surfactant and a cationic polymer to form a particle having an overall negative charge in the composition and treating said fabric with said composition.

5 The invention further provides a method of depositing a nonionic fabric softening agent onto fabric from a fabric softening composition comprising emulsifying the softening agent with an anionic surfactant and then post-dosing an aqueous solution of a cationic polymer to form a particle  
10 having an overall negative charge in the composition and treating said fabric with said composition.

In the compositions of the invention the particles formed from the fabric softening agent, the anionic surfactant and  
15 cationic polymer have an overall net negative charge. This is measured by Zeta potential measurements (e.g. as measured on a Malvern Instrument Zeta-Sizer).

It is particularly surprising that the particles deposit  
20 onto the fabric because of their overall net charge. Without wishing to be bound by theory it is believed that the above overall negatively charged particles have sufficient local positive charge associated with the polymer to allow them to deposit onto the surface of the fabric.

25

Detailed Description of the Invention

Fabric Softening Agents

- 5 -

The compositions of the invention comprise at least one fabric softening agent chosen from nonionic fabric softeners.

5 The nonionic fabric softener may be any such suitable softener, but, particularly preferred nonionic softeners are the CPE and RSE compounds as defined herein.

In the context of the present invention the initials CPE or 10 RSE stand for a liquid or soft solid derivative of a cyclic polyol or a reduced saccharide respectively which results from 35 to 100% of the hydroxyl groups of the cyclic polyol or reduced saccharide being esterified and/or etherified, the CPE or RSE having two or more ester or ether groups 15 independently attached to a C<sub>8</sub> to C<sub>22</sub> alkyl or alkenyl chain.

The CPE or RSE used according to the invention does not have any substantial crystalline character at 20°C. Instead it is preferably in a liquid or soft solid state as herein 20 defined at 20°C.

The liquid or soft solid (as hereinafter defined) CPEs or RSEs of the present invention result from 35 to 100% of the hydroxyl groups of the starting cyclic polyol or reduced 25 saccharide being esterified or etherified with groups such that they are in the requisite liquid or soft solid state.

Typically the CPE's or RSE's have 3 or more ester or ether groups or mixtures thereof, for example 3 to 8, eg 3 to 5. 30 Preferably the CPE or RSE has 4 or more ester or ether

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groups. It is preferred if two or more of the ester or ether groups of the CPE or RSE are independently of one another attached to a C<sub>8</sub> to C<sub>22</sub> alkyl or alkenyl chain. The C<sub>8</sub> to C<sub>22</sub> alkyl or alkenyl groups may be branched or linear

5 carbon chains.

Preferably 35 to 85% of the hydroxyl groups of the cyclic polyol or reduced saccharide, most preferably 40 to 80%, even more preferably 45 to 75%, such as 45 to 70% are

10 esterified or etherified.

Preferably the CPE or RSE contains 35% tri or higher esters, eg at least 40%.

15 CPEs are preferred for use with the present invention. Inositol is a preferred example of a cyclic polyol. Inositol derivatives are especially preferred.

20 In the context of the present invention the term cyclic polyol encompasses all forms of saccharides. Indeed saccharides are especially preferred for use with this invention. Examples of preferred saccharides from which the CPE's or RSE's may be derived are monosaccharides and disaccharides.

25 Examples of monosaccharides include xylose, arabinose, galactose, fructose, sorbose and glucose. Glucose is especially preferred. Examples of disaccharides include maltose, lactose, cellobiose and sucrose. Sucrose is

30 especially preferred.

An example of a reduced saccharide is sorbitan.

The liquid or soft solid CPE's or RSE's of the present invention can be prepared by a variety of methods well known to those skilled in the art. These methods include acylation of the cyclic polyol or reduced saccharide with an acid chloride; trans-esterification of the cyclic polyol or reduced saccharide fatty acid esters using a variety of catalysts; acylation of the cyclic polyol or reduced saccharide with an acid anhydride and acylation of the cyclic polyol or reduced saccharide with a fatty acid. Typical preparations of these materials are disclosed in US 4 386 213 and 14416/88 (Procter and Gamble).

15 If the CPE is a disaccharide it is preferred if the disaccharide has 3 or more ester or ether groups. Particularly preferred CPE's are esters with a degree of esterification of 3 to 5, for example, sucrose tri, tetra and penta esters.

20 Where the cyclic polyol is a reducing sugar it is advantageous if each ring of the CPE has one ether group, preferably at the C<sub>1</sub> position. Suitable examples of such compounds include methyl glucose derivatives.

25 Examples of suitable CPEs include esters of alkyl(poly)glucosides, in particular alkyl glucoside esters having a degree of polymerisation from 1 to 2.

30 The liquid or soft solid CPE's or RSE's of the present invention are characterised as materials having a

solid:liquid ratio of between 50:50 and 0:100 at 20°C as determined by T<sub>2</sub> relaxation time NMR, preferably between 43:57 and 0:100, most preferably between 40:60 and 0:100, such as, 20:80 and 0:100. The T<sub>2</sub> NMR relaxation time is 5 commonly used for characterising solid:liquid ratios in soft solid products such as fats and margarines. For the purpose of the present invention, any component of the NMR signal with a T<sub>2</sub> of less than 100 microsecond is considered to be a solid component and any component with T<sub>2</sub> is greater than 10 100 microseconds is considered to be a liquid component. For the CPE's and RSE's the tetra, penta etc prefixes only indicate the average degrees of esterification. The compounds exist as a mixture of materials ranging from the monoester to the fully esterified ester. It is the average 15 degree of esterification which is used herein to define the CPE's and RSE's.

The HLB of the CPE or RSE is typically between 1 and 3. 20 Factors governing the suitability of the CPE's and RSE's are the presence and degree of branched chains, mixed chain lengths and the level of unsaturation. It has been found that CPE's and RSE's having unsaturated or 25 mixed alkyl chain lengths are particularly preferred.

The CPEs and RSEs for use in the invention include those recited in the following examples, including sucrose pentalaurate, sucrose tetraoleate, sucrose pentaerucate,

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sucrose tetraerucate, and sucrose pentaoleate. Suitable materials include some of the Ryoto series available from Mitsubishi Kagaku Foods Corporation.

5 Other nonionic fabric softening agents that may be used in the compositions include pentaerythritol esters, and sorbitan esters, mono, di and triglycerides, ester oils, mineral oils, fatty acids, fatty alcohols and alkyl polyglycosides.

10

The fatty acid may be a C<sub>8</sub>-C<sub>24</sub> alkyl or alkenyl monerocarboxylic acid. Preferably the fatty acid is saturated. The fatty alcohols may have the same chain length as above.

15

Mixtures of any of the aforementioned types of nonionic fabric softening agents may be used.

20 The fabric softening agent is present in the composition preferably in total amount of 0.5% - 80%, by weight based upon the total weight of the composition, more preferably 0.5% - 50%, more preferably 1 - 30%, more preferably as 2 - 25%, eg 3 - 20%.

25 Anionic Surfactant

The anionic surfactant may be any suitable anionic surfactant conventionally used in laundry compositions.

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The anionic surfactant may be chosen from soap and non-soap anionic surfactants and mixtures thereof.

Many suitable detergent active compounds are available and 5 are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

Anionic surfactants are well-known to those skilled in the 10 art. Examples include alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C<sub>8</sub>-C<sub>15</sub>; primary and secondary alkylsulphates, particularly C<sub>8</sub>-C<sub>15</sub> primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; 15 dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

The compositions preferably comprise 0.1% - 10% by weight anionic surfactant, more preferably 0.2% - 5%, most 20 preferably 0.5% - 3.5%.

The weight ratio of fabric softening agent to anionic surfactant is preferably in the range 15:1 to 1:10, more 25 preferably 10:1 to 1:5, most preferably 10:1 to 1:1.

Nonionic Emulsifier

The compositions may optionally further comprise nonionic emulsifiers. Any nonionic emulsifier conventionally used in 30 laundry compositions may be used e.g. nonionic ethoxylated

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surfactants have an HLB of from about 10 to about 20. It is advantageous if the surfactant alkyl group contains at least 12 carbon atoms. If present the nonionic surfactant may be used in amounts of 0.1 - 10% by weight, preferably 0.2 - 5%.

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Cationic polymers

The compositions further comprise cationic polymers. Any suitable cationic polymers may be used according to the invention. The cationic polymer is believed to act as a 'bridging' polymer and aids deposition of the emulsified fabric softener particle onto the surface of the fabric being treated.

10 Suitable cationic polymers include cationic guar polymers and their derivatives (eg the Jaguar series of polymers available from Rhodia), cationic cellulose polymers and their derivatives (eg the Celquat series of polymers available from National Starch and Chemical Ltd and the Ucare series of polymers available from Amerchol), cationic starches such as potato starch (eg the SoftGel and Solvitose series of polymers available from Avebe and the C\*bond polymers series from Cerestar), and cationic chitosan and derivatives. Mixtures of such polymers may also be used.

15

20 Any of the cationic polymers recited in the following examples are suitable for use in the compositions of the invention.

25 The compositions preferably comprise 0.01-5% by weight of the cationic polymer, more preferably 0.05-4.5%, most preferably 0.1-3.5%, eg 0.1-3%.

30 The compositions comprise no more than 1% by weight in total of non-polymeric cationic surfactant and/or cationic fabric

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softening compounds. Preferably the compositions are substantially free of said cationic materials.

If a cationic surfactant or cationic softening compound, eg 5 a quaternary ammonium compound, is present in the composition it is preferred that it is present in an amount of 0.75% by weight or less, preferably 0.5% or less such as 0.2% by weight or less.

10 In the compositions the weight ratio of the softening agent to the cationic polymer is preferably within the range 100:1 to 1:1, preferably 40:1 to 1:1, e.g. 10:1 to 1:1.

In the compositions the weight ratio of the softening agent 15 to the total amount of anionic surfactant and cationic polymer is preferably within the range 15:1 to 1:10, more preferably 10:1 to 1:5, most preferably 10:1 to 1:1.

#### Other Polymers

20 Nonionic polymers may optionally be present in the compositions in addition to the cationic polymers. Suitable nonionic polymers that may optionally be present include the Pluronic series of polymers available from BASF, dialkyl 25 PEGs, cellulose derivatives as described in GB 213 730 (Unilever), hydroxyethyl cellulose, starch, and hydrophobically modified nonionic polyols such as Acusol 880/882 available from Rohm & Haas.

30 Anionic polymers may also be present in the composition.

Optional ingredients

The compositions may also contain one or more optional ingredients, selected from oils, (such as vegetable oils and ester oils) electrolytes, non-aqueous solvents, pH buffering agents, perfumes, perfume carriers, fluorescers, colorants, hydrotropes, antifoaming agents, antiredeposition agents, polymeric and other thickeners, enzymes, optical brightening agents, opacifiers, anti-shrinking agents, anti-wrinkle agents, anti-spotting agents, germicides, fungicides, anti-oxidants, anti-corrosion agents, drape imparting agents, antistatic agents, sunscreens, colour care agents and ironing aids.

If the product is a liquid, a viscosity control agent may be included. Any viscosity control agent typically used with rinse conditioners is suitable, for example biological polymers such as Xanthum gum (Kelco ex Kelsan and Rhodopol ex Rhone-Poulenc). Synthetic polymers may also be used as viscosity control agents eg polyacrylic acid, poly vinyl pyrrolidone, polyethylene, carbomers, polyethylene and polyethylene glycols.

It is preferred that the compositions are substantially free of bleaches. It is especially preferred that the compositions are entirely free of bleaches.

**Product Form**

The compositions may be in any form conventionally used for fabric softening compositions for example, powder, paste,

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gel or liquid. It is preferred if the product is a liquid and especially an emulsion.

The compositions may be prepared by any suitable method.

One method (method A) is to dissolve the cationic polymer in 5 water, optionally with heating to assist dissolution, and then add the anionic surfactant. The solution initially becomes cloudy but clears when the polymer / surfactant complex re-dissolves. After this point the nonionic softener is added.

10

Another method (method B) is to emulsify the nonionic fabric softener with the anionic surfactant and then to post-dose an aqueous solution of the cationic polymer to this emulsion. A further method (method C) is to solubilise the 15 polymer in solution and then add the anionic surfactant/ nonionic softener as a co-melt.

#### Examples

20 The invention is illustrated by the following non-limiting examples. Further examples within the scope of the present invention will be obvious to the man skilled in the art.

25 Samples of the invention are denoted by a number and comparative samples are denoted by a letter.

#### Example 1

30 Compositions 1 to 24 in the table below were prepared by method A. All % are by weight as the active ingredient.

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Compositions A and B were prepared by dissolving the anionic surfactant in water, followed by adding the nonionic softener and mixing the composition for 10 minutes.

Sample No.	Cationic Polymer Type and % by weight	Anionic surfactant type and % by weight	Fabric softener type and % by weight
1	A-0.05%	ABS-2%	ER290-4.5%
2	A-0.1%	ABS-2%	ER290-4.5%
3	B-0.1%	ABS-1%	ER290-4.5%
4	C-0.3%	ABS-1%	ER290-4.5%
5	C-0.4%	ABS-1%	ER290-4.5%
6	C-0.5%	ABS-1%	ER290-4.5%
7	C-0.7%	ABS-1%	ER290-4.5%
8	C-0.8%	ABS-1%	ER290-4.5%
9	C-0.9%	ABS-1%	ER290-4.5%
10	C-1.0%	ABS-1%	ER290-4.5%
11	C-1.5%	ABS-0.8%	ER290-4.5%
12	D-0.1%	ABS-1%	ER290-4.5%
13	D-0.2%	ABS-1%	ER290-4.5%
14	D-0.3%	ABS-1%	ER290-4.5%
15	E-0.1%	ABS-1%	ER290-4.5%
16	E-0.2%	ABS-1%	ER290-4.5%
17	E-0.3%	ABS-1%	ER290-4.5%
18	F-1.5%	SDS-0.75%	ER290-4.5%
19	F-2.0%	SDS-0.75%	ER290-4.5%
20	A-0.3%	ABS-3%	ER290-15%
21	C-3.0%	ABS-3%	ER290-15%
22	C-2.0%	G-0.50%	ER290-4.5%
23	C-1.5%	G-2.0%	ER290-2.5%
24	C-1.5%	G-3.5%	ER290-1.0%
A	--	G-2.0%	ER290-2.3%
B	--	G-3.0%	ER290-1.5%

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Polymer type A was Jaguar C13-S from Rhodia; a cationic guar gum.

Polymer type B was Jaguar C162 from Rhodia; a cationic guar gum.

5 Polymer type C was Softgel BDA from Avebe; a cationic potato starch.

Polymer type D was Ucare JR125 from Amerchol; a cationic cellulose.

10 Polymer type E was Ucare JR400 from Amerchol; a cationic cellulose.

Polymer type F was Solvitose from Avebe; a cationic starch.

ABS is sodium dodecyl benzene sulphonate from Aldrich.

SDS is sodium dodecyl sulphate from Aldrich.

15

G is sodium cocoyl isothionate from Akzo

ER290 is Ryoto ER290 (sucrose tetraerucate) available from Mitsubishi Kagaku Foods Corporation.

20

The compositions were all homogeneous in appearance. The particles formed from the cationic polymer, anionic surfactant and fabric softener had a net overall negative charge.

25

Example 2

Samples 6-10, 22, A and B and a commercial dilute fabric softening composition, C, were tested for fabric softening

30 ability. To simulate the effects of carryover of anionic surfactant from the wash various amounts of 1% by weight

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solution of alkyl benzene sulphonate were added to the rinse liquor to determine how resistant the compositions are to such anionic carryover.

5 Softness Evaluation

Softening performance was evaluated by adding 0.1g of fabric softening compound (2ml of a 5% a.d. dispersion for liquids) to 1 litre of tap water, at ambient temperature in a 10 tergotometer. Three pieces of terry towelling (8cm x 8cm, 40g total weight) were added to the tergotometer pot. The cloths were treated for 5 minutes at 65 rpm, spin dried to remove excess liquor and line dried overnight and conditioned at 21°C/65°C.

15 Softening of the fabric was assessed by an expert panel of 4 people using a round robin paired test protocol. Each panel member assessed four sets of test cloths. Each set contained one cloth of each sample under evaluation. Panel 20 members were asked to assess softness on a nine point scale. In the table below a score of 1 represents a very soft fabric and 9 represents a very harsh fabric. Softness scores were calculated using an 'Analysis of Variance technique.

25 The softening results are given below.

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Sample No.	No of mls of 1% ABS added to replicate increasing levels of anionic carryover				
	0	1	2	3	4
6	4.75	4.25	3.75	3	4.25
7	-	3.0	2.75	2.5	2
8	-	2.5	2.75	2.75	3
9	-	3.0	3.5	2.75	3.5
10	3.75	4	3.75	3.75	4.0
22	3.9	-	-	4.6	-
A			5.9		
B			6.8		
C <sup>a</sup>			3.9		

<sup>a</sup> dilute Comfort (commercially available June 1999)

5 The above results demonstrate that the compositions of the invention provide excellent softening results at various levels of simulated anionic carryover. The compositions also did not significantly decrease the absorbency of the treated fabric.

10

The results also show that, at 2mls carryover, the compositions of the invention provided significantly better softening than the comparative composition which lacked a cationic polymer, and better softening than a commercially

15 available dilute fabric softening composition

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Example 3

A fully formulated fabric softening composition as according to the present invention was prepared as below:

5

	% by weight
ABS	1.0
Sucrose ester oil	4.5
Softgel BDA	1.0
Dye	0.0025
Perfume	0.3
Minors	0.02
Water	balance

10 The sucrose ester oil was Ryoto ER290 available from Mitsubishi Kagaku Foods Corporation. ABS and Softgel BDA are described above.

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Example 4

A second fully formulated fabric softening composition was prepared as below:

5

	% by weight
ABS	0.4
Sucrose ester oil	15.4
Softgel BDA	2.0
Dye	0.0025
Perfume	0.96
Nonionic emulsifier	1.6
Minors	0.15
Water	Balance

The sucrose ester oil was Ryoto ER290, described above. The nonionic emulsifier was coco alcohol (15 EO).

10

The composition was prepared as follows:

An aqueous solution comprising 20wt% of the nonionic emulsifier and the ABS (in a 4:1 weight ratio) was firstly 15 mixed with 30.84g of the sucrose ester oil and perfume under stirring, to form a water in oil emulsion.

Then 50g of the Softgel BDA at 8wt% was stirred into the emulsion followed by 98.36g of cold demineralised water 20 (also added under stirring). Finally the dye (0.5g) and the minors were added and stirring was continued for a further 10 minutes.

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The composition was monitored for 12 weeks, during which time it remained stable and homogenous.

Example 5

5

The table below shows the T2 NMR solid:liquid ratio of CPE's and RSE's used according to the present invention. The ratios were measured at 20°C. The degree of esterification/etherification is stated.

10

Material	Solid:liquid ratio at 20°C	Degree and % of esterification		Physical form
Ryoto 0-170 <sup>1</sup>	0:100	5/8	62.5%	Liquid
Ryoto ER-290 <sup>2</sup>	0:100	4/8	50%	Liquid
Ryoto ER-190 <sup>3</sup>	0:100	5/8	50%	Soft solid
Ryoto POS-135 <sup>4</sup>	30:70	5/8	62.5%	Soft solid
Ryoto L-195 <sup>5</sup>	43:57	5/8	62.5%	Liquid
Sucrose tetraoleate	0:100	4/8	50%	Liquid
Sucrose octaoleate	0:100	8/8	100%	Liquid

1 = sucrose pentaoleate

2 = sucrose tetraerucate

3 = sucrose pentaerucate

15 4 = sucrose pentatallowate

5 = sucrose pentalaurate

Example 6; Fabric Softening Compositions

The following example shows compositions according to the invention comprising various nonionic fabric softening 5 agents.

The compositions were prepared by firstly adding the cationic polymer (hot) to water followed by adding the molten nonionic softener/anionic surfactant mixture thereto. The only exception to this was sample 1, where the 10 subsequent order of addition was SLES followed by the sucrose monoester (coco/tallow chains).

In the samples where either Na soap or K soap is present (samples 2-5), this was achieved through in-situ 15 neutralisation of HT fatty acid by either NaOH or KOH respectively. In these cases the NaOH or the KOH was added after the polymer and before the co-melted actives.

Ingredient	sample 1	sample 2	sample 3	sample 4	sample 5
Hardened tallow fatty acid <sup>2</sup>	0	2.17%	1.58%	1.59%	1.56%
Hardened tallow Na soap	0	2.51%	1.97%	1.95%	0
Hardened tallow fatty alcohol <sup>3</sup>	0	0	1.1%	0	1.1%
Hardened tallow K soap	0	0	0	0	2.09%
Sucrose monoester (coco/tallow chains) <sup>1</sup>	4.5%	0	0	1.1%	0
Na laureth ether sulphate (SLES) <sup>4</sup>	0.5%	0.5%	0.5%	0.5%	0.5%
Cationic potato starch <sup>5</sup>	1%	1%	1%	1%	1%
Water	to 100%				
Softness score	4.75	4.50	4.25	4.00	4.00

1 = Sucrose monoester (coco/tallow chains) is available as Tegosoft PSE1419 (ex Goldschmidt AG)

5 2 = Hardened tallow fatty acid is available as Pristerine 4916 (ex Unichema)

- 25 -

- 3 = Hardened tallow fatty alcohol is available as Laurex CS (ex Albright & Wilson)
- 4 = Na laureth ether sulphate (SLES) is available as Elfan NS2436 (ex Akzo-Nobel)
- 5 5 = Cationic potato starch is available as Softgel BDA (ex Avebe)

Example 7; Measurement of Zeta potential

- 10 The Zeta potential of the following example was measured on a Malvern Instrument Zeta Sizer.
  - 0.75 wt% Softgel BDA (ex Avebe)
  - 0.75% wt% SDS (ex Adrich)
- 15 4.5% wt% ER290 (ex Mitsubishi Kagaku)  
Softgel BDA, SDS and ER290 are as described above.

The average zeta potential was minus 25.2 demonstrating that fabric softening particles formed from a nonionic fabric softener, an anionic surfactant and a cationic polymer have an overall net negative charge.

- 20

CLAIMS

1. A fabric softening composition comprising:

5 (i) at least one nonionic fabric softening agent, and

(ii) at least one anionic surfactant, and

(iii) at least one cationic polymer

10

wherein the particles formed from i), ii) and iii) have a net negative charge and the composition comprises no more than 1% by weight non-polymeric cationic surfactant and/or cationic fabric softening compounds.

15

2) A composition according to claim 1 wherein the nonionic fabric softener (i) comprises a liquid or soft solid derivative of a cyclic polyol (CPE) or of a reduced saccharide (RSE) resulting from 35 to 100% of the hydroxyl groups in the polyol or saccharide being esterified or etherified, the CPE or RSE having 2 or more ester or ether groups independently attached to a C<sub>8</sub>-C<sub>22</sub> alkyl or alkenyl chain.

25 3) A composition according to claim 2 wherein the CPE or RSE contains at least 35% tri or higher esters.

4) A composition according to any one of the preceding claims wherein the cyclic polyol or reduced saccharide has 30 40-80%, preferably 45 - 75%, of the hydroxyl groups esterified and/or etherified.

- 5) A composition according to any one of the preceding claims wherein the CPE or RSE has 3 or more ester or ether groups, preferably 4 or more.
- 6) A composition according to any one of the preceding claims wherein the CPE or RSE is derived from a monosaccharide or disaccharide.
- 10 7) A composition according to any one of the preceding claims comprising 0.5% - 50% by weight of the fabric softening agent, preferably 1% - 30%.
- 15 8) A composition according to any one of the preceding claims comprising 0.1% - 10% by weight of the anionic surfactant, preferably 0.2% - 5%.
- 20 9) A composition according to any one of the preceding claims wherein the cationic polymer is selected from cationic guar derivatives, cationic cellulose derivatives, cationic starch derivatives and, cationic chitosan derivatives or mixtures thereof.
- 25 10) A composition according to any one of the preceding claims comprising 0.01% - 5% by weight of the cationic polymer, preferably 0.1-3%.
- 30 11) A composition according to any one of the preceding claims wherein the weight ratio of softening agent to the total amount of anionic surfactant and cationic polymer is within the range 15:1 to 1:10, preferably 10:1 to 1:1.

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- 12) A composition according to any preceding claim which is a liquid, preferably an emulsion.
- 13) A method of depositing a nonionic fabric softening agent onto fabric from a fabric softening composition, comprising emulsifying the softening agent with an anionic surfactant and a cationic polymer to form a particle having an overall net negative charge in the composition and treating said fabric with said composition.
- 10
- 14) A method of depositing a nonionic fabric softening agent onto fabric from a fabric softening composition, comprising emulsifying the softening agent with an anionic surfactant and then post-dosing an aqueous solution of a cationic polymer to form a particle having an overall negative charge on the composition and treating said fabric with said composition.
- 15
- 16) A method according to claim 13 or claim 14 wherein the fabric softening agent is as defined in any one of the preceding claims.
- 20
- 17) A method according to either claim 14 or claim 15 wherein the cationic polymer is as defined in claim 9.

25

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 00/01706

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7 C11D1/83 C11D3/22 //C11D1:12,C11D1:14,C11D1:22

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**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category <sup>a</sup>	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 093 601 A (UNILEVER NV) 9 November 1983 (1983-11-09)	1, 9, 11-13, 15, 16
Y	page 4, line 15 -page 7, paragraph 4 page 8, line 33 -page 10, line 18 examples 12,13 claims 1,11	1-16
Y	WO 98 16538 A (UNILEVER) 23 April 1998 (1998-04-23) cited in the application page 5, line 25 -page 9, line 26 page 14, line 28 -page 15, line 30 examples 50-53 claims 1-8	1-16

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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## INTERNATIONAL SEARCH REPORT

International Application No  
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 447 643 A (KELKENBERG HEIKE ET AL) 5 September 1995 (1995-09-05) cited in the application column 1, line 60 -column 4, line 12	1,2,9, 11-16
A	DE 197 03 362 C (HENKEL KGAA) 20 November 1997 (1997-11-20) page 2, line 36 -page 3, line 14 page 4, line 47 -page 5, line 65 examples 1-8	1,7-16
A	US 5 419 842 A (CRUTZEN ANDRE) 30 May 1995 (1995-05-30) column 3, line 50-61 column 7, line 47 -column 8, line 14 examples 1,2	1,7,8, 11-13,15

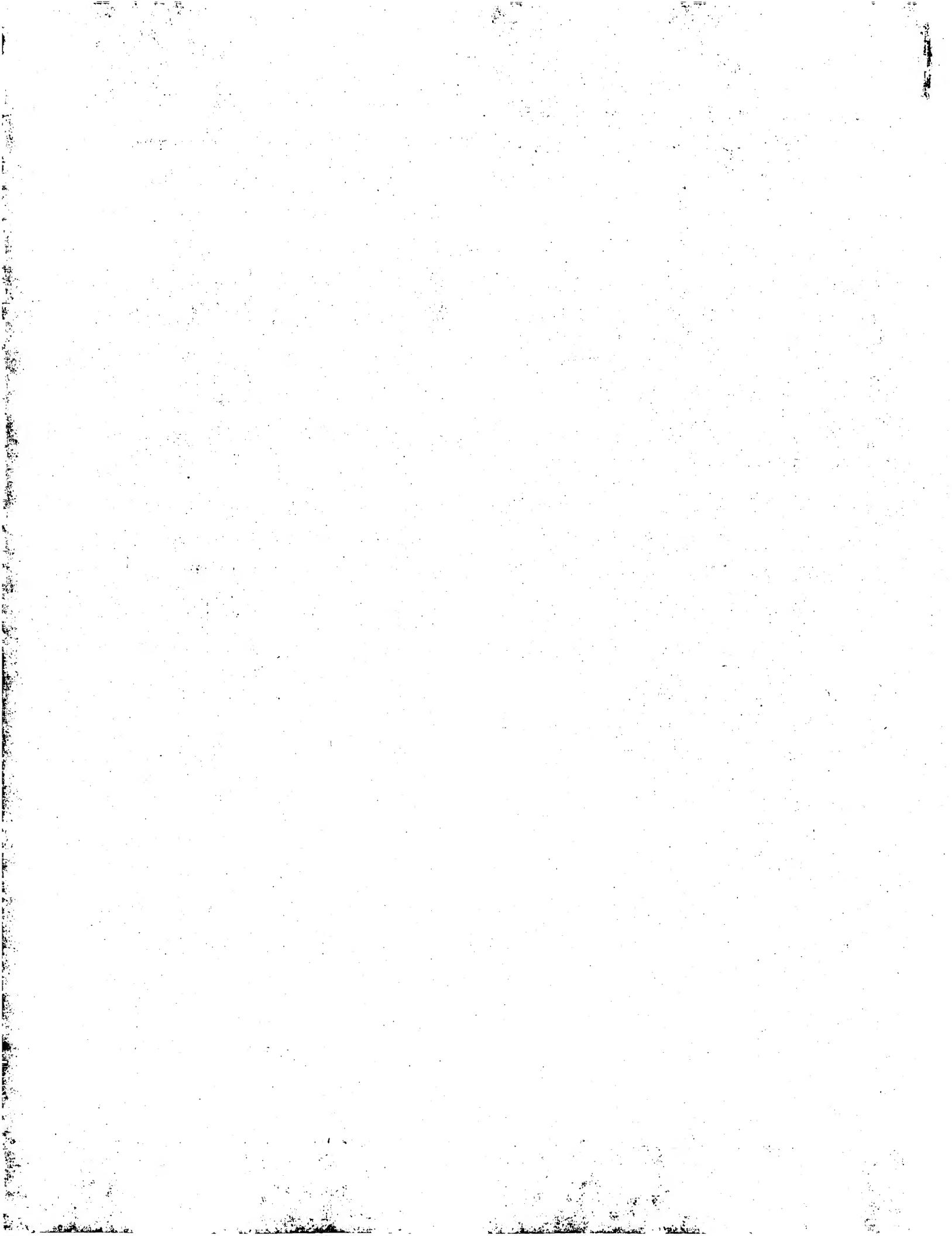
# INTERNATIONAL SEARCH REPORT

Information on patent family members

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Reclamation, Mumbai400 020, Maharashtra (IN).(72) Inventors: CLARKE, David, Ellis; 48 Keswick Avenue,  
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WO 00/71806 A1

(54) Title: FABRIC SOFTENING COMPOSITIONS

(57) Abstract: A fabric softening composition comprising: (a) a cationic fabric softening compound; and (b) an emulsified silicone. In one aspect the viscosity of the silicone before emulsification is from 10,000cSt to 1,000,000cSt, preferably from 30,000cSt to 750,000cSt, more preferably from 40,000cSt to 400,000cSt, most preferably 45,000cSt to 250,000cSt, e.g. 45,000cSt to 200,000cSt and the emulsion is a macro-emulsion. In another aspect, the median silicone droplet size in the emulsion is at least 0.2μm, preferably at least 0.25μm, more preferably at least 0.39μm, preferably also no greater than 25μm and is emulsified with an emulsifier comprising one or more cationic surfactants.

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FABRIC SOFTENING COMPOSITIONS

Technical Field

5 The present invention relates to fabric softening compositions which provide additional benefits to the fabric, particularly improved crease reduction and/or ease of ironing.

10 Background and Prior Art

Fabric softener compositions, especially those added in the rinse, are well known. It is also known to incorporate one or more additional materials such as silicones, to reduce 15 wrinkling of the fabric during the rinsing and drying stages of the wash. For example WO-A-96/15309 discloses the use of a combination of a silicone and a film-forming polymer for this purpose. Typical silicones in this application are polydiorganosiloxanes. Nevertheless, there remains a need in 20 fabric softening compositions to formulate with additives which not only reduce the appearance of wrinkles or creases before ironing, but also make ironing easier.

In many prior art compositions, the silicones are 25 incorporated in the form of an emulsion, which is a micro-emulsion, that is to say the silicone is present as liquid droplets having a droplet size less than the wavelength of visible light and so the emulsion is substantially transparent. However, in a few cases, they are macro- 30 emulsions (e.g. WO-A-97/31997 and 98). The silicones before emulsification are those having relatively low

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viscosities, because it is assumed that those with higher viscosities are more difficult to handle during the process of manufacturing the product and are less suited for anti-creasing performance. WO-A-95/24460 discloses a fabric 5 softening composition which contains from about 0.2% to about 20% of a polydimethyl siloxane having a viscosity from about 2 to 5,000 centi-Stokes (cSt).

It has now been discovered that, surprisingly, good anti-10 creasing and/or ease of ironing can be achieved by formulating with a silicone which is incorporated in the form of a macro-emulsion and which silicone has a viscosity of from 10,000cSt to 1,000,000cSt, and/or the emulsified silicone has a median droplet size of at least 0.2 $\mu$ m and is 15 emulsified with at least one cationic surfactant.

#### Definition of the Invention

Thus according to a first aspect of the invention there is 20 provided a fabric softening composition comprising:-  
(a) a cationic fabric softening agent; and  
(b) an emulsified silicone;  
wherein the viscosity of the silicone before emulsification is from 10,000cSt to 1,000,000cSt, preferably from 30,000cSt 25 to 750,000cSt, more preferably from 40,000cSt to 400,000cSt, most preferably 45,000cSt to 250,000cSt, eg, 45,000cSt to 200,000cSt, and the emulsion is a macro-emulsion.

A second aspect of the present invention provides a fabric 30 softening composition comprising:-  
(a) a cationic fabric softening agent; and

- 3 -

(b) an emulsified silicone;

wherein the median droplet size of the silicone in the emulsion is  $0.2\mu\text{m}$ , preferably at least  $0.25\mu\text{m}$ , more preferably at least  $0.39\mu\text{m}$ , preferably also no greater than 5  $25\mu\text{m}$  and is emulsified with an emulsifier comprising one or more cationic surfactants.

A third aspect of the present invention provides a method of manufacturing a fabric softening composition, the method 10 comprising obtaining a macro-emulsion of a silicone having a viscosity of from 10,000cSt to 1,000,000cSt and admixing said macro-emulsion with a cationic fabric softening agent.

A fourth aspect of the present invention provides a method 15 of manufacturing a fabric softening composition, the method comprising obtaining the emulsion in the form of an emulsion of a silicone having a viscosity of from 10,000cSt to 1,000,000cSt, preferably from 30,000cSt to 750,000cSt, more preferably from 40,000cSt to 400,000cSt, most preferably 20 45,000cSt to 250,000cSt, eg 45,000cSt to 200,000cSt the median droplet size of the silicone in the emulsion being at least  $0.2\mu\text{m}$ , preferably at least  $0.25\mu\text{m}$ , more preferably at least  $0.39\mu\text{m}$ , preferably also no greater than  $25\mu\text{m}$  and is emulsified with an emulsifier comprising one or more 25 cationic surfactants, and admixing said emulsion with a cationic fabric softening agent.

Compositions according to the present invention may 30 optionally embody both the first and second aspects of the present invention and processes for their manufacture optionally may embody the third and fourth aspects. A

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method of using a composition according to the first and/or second aspects of the present invention by applying it to a fabric or textile for softening the fabric or textile, constitutes another aspect of the invention.

5

For the avoidance of doubt, in the context of the present invention, the term emulsified silicone means that the silicone is in emulsion form prior to incorporation in the fabric softening composition and does not necessarily remain 10 in that form in the final product.

The cationic fabric softening agent may comprise one or more cationic fabric softening materials and the emulsified silicone may comprise one or more individual silicone 15 materials.

#### Detailed Description of the Invention

##### Cationic Fabric Softening Agents

20

Preferably, the cationic fabric softening agent is a quaternary ammonium material or a quaternary ammonium material containing at least one ester group. The quaternary ammonium compounds containing at least one ester group are 25 referred to herein as ester-linked quaternary ammonium compounds.

As used herein the term ester group, when used as a group in the quaternary ammonium material, includes an ester group 30 which is a linking group in the molecule.

- 5 -

It is preferred for the ester-linked quaternary ammonium compounds to contain two or more ester groups. In both monoester and the diester quaternary ammonium compounds it is preferred if the ester group(s) is a linking group 5 between the nitrogen atom and an alkyl group. The ester group(s) is preferably attached to the nitrogen atom via another hydrocarbyl group.

Also preferred are quaternary ammonium compounds containing 10 at least one ester group, preferably two, wherein at least one higher molecular weight group containing at least one ester group and two or three lower molecular weight groups are linked to a common nitrogen atom to produce a cation and wherein the electrically balancing anion is a halide, 15 acetate or lower alkylsulphate ion, such as chloride or methosulphate. The higher molecular weight substituent on the nitrogen is preferably a higher alkyl group, containing 12 to 28, preferably 12 to 22, e.g. 12 to 20 carbon atoms, such as coco-alkyl, tallowalkyl, hydrogenated tallowalkyl or 20 substituted higher alkyl, and the lower molecular weight substituents are preferably lower alkyl of 1 to 4 carbon atoms, such as methyl or ethyl, or substituted lower alkyl. One or more of the said lower molecular weight substituents may include an aryl moiety or may be replaced by an aryl, 25 such as benzyl, phenyl or other suitable substituents.

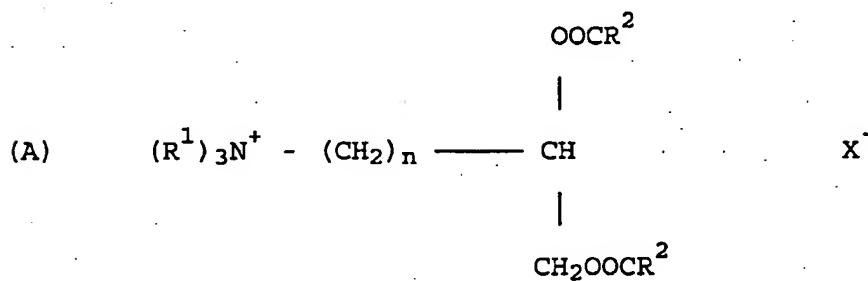
Preferably the quaternary ammonium material is a compound having two C<sub>12</sub>-C<sub>22</sub> alkyl or alkenyl groups connected to a quaternary ammonium head group via at least one ester link, 30 preferably two ester links or a compound comprising a single

- 6 -

long chain with an average chain length equal to or greater than C<sub>20</sub>.

More preferably, the quaternary ammonium material comprises  
5 a compound having two long chain alkyl or alkenyl chains  
with an average chain length equal to or greater than  $C_{14}$ .  
Even more preferably each chain has an average chain length  
equal to or greater than  $C_{16}$ . Most preferably at least 50%  
of each long chain alkyl or alkenyl group has a chain length  
10 of  $C_{18}$ . It is preferred if the long chain alkyl or alkenyl  
groups are predominantly linear.

The most preferred type of ester-linked quaternary ammonium material that can be used in compositions according to the invention is represented by the formula (A):



wherein each  $R^1$  group is independently selected from C<sub>1-4</sub> alkyl, hydroxyalkyl or C<sub>2-4</sub> alkenyl groups; and wherein each 25  $R^2$  group is independently selected from C<sub>8-28</sub> alkyl or alkenyl groups; X<sup>-</sup> is any suitable counter-ion, i.e. a halide, acetate or lower alkylsulphate ion, such as chloride or methosulphate.

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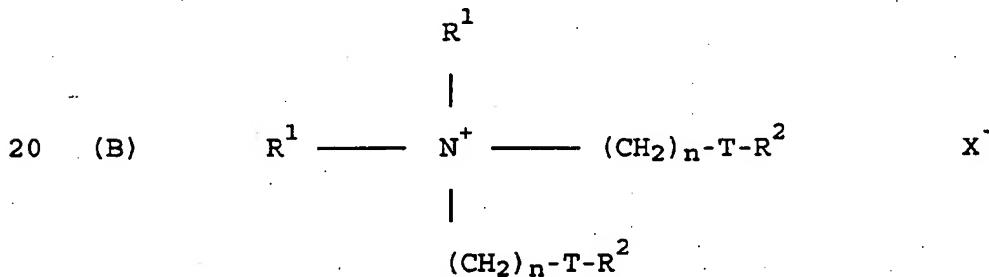
n is an integer from 1-5 or is 0

It is advantageous for environmental reasons if the quaternary ammonium material is biologically degradable.

5

Preferred materials of this class such as 1,2 bis[hardened tallowoxyloxy]-3-trimethylammonium propane chloride and their method of preparation are, for example, described in US-A-4 137 180. Preferably these materials comprise small amounts 10 of the corresponding monoester as described in US-A-4 137 180 for example 1-hardened tallow-oxyloxy-2-hydroxy-3-trimethylammonium propane chloride.

Another class of preferred ester-linked quaternary ammonium 15 materials for use in compositions according to the invention can be represented by the formula (B):



wherein  $R^1$ , n,  $R^2$  and  $X^-$  are as defined above.

25



and T is -O-C- or -C-O-; and

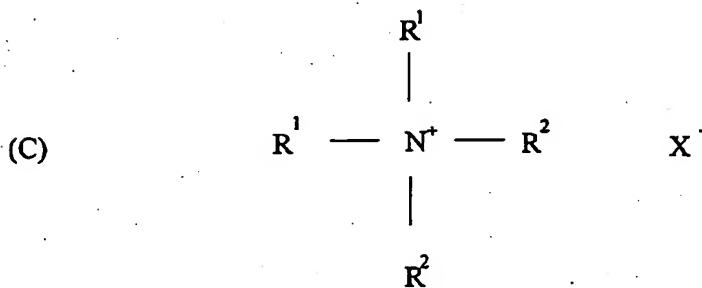
30

- 8 -

It is especially preferred that each  $R^1$  group is methyl and each  $n$  is 2.

Of the compounds of formula (B), Di-(tallowyloxyethyl)-5 dimethyl ammonium chloride, available from Hoechst, is the most preferred. Di-(hardened tallowyloxyethyl)dimethyl ammonium chloride, ex Hoechst and di-(tallowyloxyethyl)-methyl hydroxyethyl methosulphate are also preferred.

10 Another preferred class of quaternary ammonium cationic fabric softening agent is defined by formula (C) :-



15 where  $R^1$ ,  $R^2$  and  $X^-$  are as hereinbefore defined.

A preferred material of formula (C) is di-hardened tallow-diethyl ammonium chloride, sold under the Trademark Arquad 2HT.

20 The optionally ester-linked quaternary ammonium material may contain optional additional components, as known in the art, in particular, low molecular weight solvents, for instance isopropanol and/or ethanol, and co-actives such as nonionic 25 softeners, for example fatty acid or sorbitan esters.

The fabric softening agent is present in the composition preferably in a total amount of 0.5% - 50% by weight based upon the total weight of the composition, more preferably 5 0.5% to 35%, more preferably 1-30%, more preferably 3-25%, most preferably 3-20%, eg 8-20%.

Emulsified Silicone

- 10 According to the first and third aspects of the present invention, in the emulsified silicone, the silicone droplets are incorporated to be in the form of a macro-emulsion, that is to say the droplets have a median size in the wavelength range corresponding to the visible spectrum, or even larger.
- 15 Preferably, the emulsion is an oil-in-water emulsion. The term median size refers to the number average. The visible spectrum is  $0.39\mu\text{m}$  to  $0.77\mu\text{m}$ . In the emulsion, the silicone droplets are then preferably from  $0.39\mu\text{m}$  to  $25\mu\text{m}$ . In the second and fourth aspects of the present invention,
- 20 in the emulsion, the silicone droplets have a median size of at least  $0.2\mu\text{m}$ , preferably at least  $0.25\mu\text{m}$ . The droplet size may be determined based on measurements of median DV05 using a Malvern X Mastersizer.
- 25 The silicone may be of any structure which gives rise to one or more of the desired benefits in use of the fabric softener formulation. Preferably, it has a linear structure. It is preferably a non-functional silicone, especially one which is non-amino functional. Typical 30 silicones are siloxanes which have the general formula  $\text{R}_a\text{SiO}_{(4-a)/2}$  wherein each R is the same or different and is

- 10 -

selected from hydrocarbon and hydroxyl groups, 'a' being from 0 to 3 and in the bulk material; 'a' has an average value of from 1.85-2.2.

5 Most preferably, the silicone is a polydi-C<sub>1-6</sub>alkyl (preferably a polydimethyl) siloxane end-terminated either by tri-C<sub>1-6</sub> alkylsilyl (e.g. trimethylsilyl) or hydroxy-di-C<sub>1-6</sub> alkylsilyl (e.g. hydroxy-dimethylsilyl) groups, or by both.

10

Certainly, in the case of compositions according to the first and third aspects of the present invention and preferably, in the case of compositions according to the second and fourth aspects, the silicone has a viscosity 15 before emulsification (as measured on a Brookfield RV4 viscometer at 25°C using spindle No.4 at 100 rpm) of from 10,000cSt to 1,000,000cSt, preferably from 30,000cSt to 750,000cSt, more preferably from 40,000cSt to 400,000cSt, most preferably 45,000cSt to 250,000cSt, eg 45,000cSt to 20 200,000 cSt.

Preferably, in compositions according to the first and third aspects of the present invention and certainly in those according to the second and fourth aspects of the invention, 25 emulsification is effected using one or more cationic surfactants, preferably having a non-halogen counter-ion.

The cationic emulsifiers are believed to enhance deposition of the silicone during use of the fabric softening 30 composition. Preferred counter-ions include methosulphate,

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ethosulphate, tosylate, phosphate and nitrate. If a halogen counter-ion is used, it is preferably chloride.

For example, mixtures of one or more cationic and one or 5 more nonionic surfactants can be used, or even nonionic surfactant(s) alone.

Preferably, the total of amount of emulsifying surfactant(s) is from 0.5% to 20%, preferably from 2% to 12%, more 10 preferably from 3% to 10% by weight of the emulsion.

The emulsified silicone (as 100% active silicone) may be included in the fabric softener compositions in an amount of 3.5% to 15% by weight of the total composition (including 15 the emulsion product containing the silicone emulsion), preferably 3.75% to 12%, more preferably 4% to 10%, most preferably 4.5% to 10%. However, it may be possible to include up to 20% by weight if it can be incorporated into the fabric softening composition without instability 20 occurring therein. The total amount of silicone in the emulsion will generally be up to 70% by weight of the emulsion.

Preferably, the weight ratio of silicone to total 25 emulsifying surfactant(s) is from 2.3:1 to 120:1, more preferably 3:1 to 120:1, for example from 3:1 to 30:1. Typical cationic surfactants are alkyl tri-methylammonium methosulphates and derivatives in which at least two of the methyl groups on the nitrogen atom are replaced by 30 (poly)alkoxylated groups.

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In the final product, the weight ratio of total fabric softening agent to total silicone is from 1:1 to 70:1, more preferably from 1.5:1 to 25:1, more preferably 2.5:1 to 10:1, eg 3:1 to 7:1.

5

Perfume

The compositions may comprise perfume. If present, the level of perfumes in the compositions may be 0.25% to 2% by 10 weight, preferably 0.27% to 2%, such as 0.3% to 1.5%.

Optional ingredients

The compositions may also contain one or more optional 15 ingredients, selected from electrolytes, non-aqueous solvents, pH buffering agents, perfume carriers, fluorescers, colorants, hydrotropes, antifoaming agents, antiredeposition agents, polymeric and other thickeners, enzymes, optical brightening agents, opacifiers, anti- 20 shrinking agents, auxiliary anti-wrinkle agents, anti-spotting agents, germicides, fungicides, anti-oxidants, anti-corrosion agents, drape imparting agents, antistatic agents, sunscreens, colour care agents and auxiliary ironing aids.

25

The preferred product form is a liquid, more especially an aqueous liquid. In liquid products, a viscosity control agent may be included. Any viscosity control agent typically used with rinse conditioners is suitable, for 30 example biological polymers such as Xanthum gum (Kelco ex Kelsan and Rhodopol ex Rhone-Poulenc). Synthetic polymers

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may also be used as viscosity control agents e.g. polyacrylic acid, poly vinyl pyrrolidone, polyethylene, carbomers, polyethylene, polyethylene glycols and cellulose-based thickeners such as hydroxy-ethyl cellulose modified to 5 include long chain substituent groups. Also suitable as viscosity modifiers are decoupling polymers and deflocculating polymers.

It is preferred that the compositions are substantially free 10 of bleaches.

#### **Product Form**

However, the compositions may be in any form conventionally 15 used for fabric softening compositions for example, powder, paste or gel. It is preferred if the final product itself is a liquid and especially an aqueous emulsion, preferably a macro-emulsion and not a micro-emulsion, containing suspended fabric softener and emulsified silicone droplets.

20

#### **Compositions**

A fabric softening composition within the scope of the present invention may comprise 8 to 50% by weight of a 25 cationic fabric softening agent; and perfume; and 3.5 to 15% by weight of an emulsified silicone (all weights being of the total weight of the composition) the silicone having been emulsified with one or more cationic surfactants to form a macro-emulsion with the viscosity of the silicone 30 before emulsification being from 10,000cSt to 400,000cSt,

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preferably from 20,000cSt to 350,000cSt, more preferably from 25,000cSt to 250,000cSt.

Another fabric softening composition with the scope of the  
5 invention may comprise 8 to 50% by weight of a cationic  
fabric softening agent; and perfume; and 3.5 to 15% by  
weight of an emulsified silicone (all weights being of the  
total weight of the composition) the median droplet size of  
the emulsified silicone being at least 0.2 $\mu$ m, preferably at  
10 least 0.25 $\mu$ m, more preferably at least 0.39 $\mu$ m, preferably  
also no greater than 25 $\mu$ m and the silicone being emulsified  
with an emulsifier comprising one or more cationic  
surfactants.

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Examples

Example A

5 A dimethyl-terminated polydimethylsiloxane (PDMS) having a viscosity of 60,000cSt was formulated as an aqueous emulsion thus in

	<u>Component</u>	<u>% wt</u>
10	PDMS	60
	COCOTMAMS (1)	3.5
	COCOPEMAMS (2)	1.9
	Water, preservatives	to 100
15		
	(1) coconut trimethylammonium methosulphate	
	(2) coconut pentaethoxymethylammonium methosulphate	

Examples 1 and 2

20 The emulsion of Example A was included in dilute (Example 1) and concentrate (Example 2) forms of fabric softener compositions, in which amounts are % by weight of the total composition:-

25

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	<u>Component</u>	<u>Example 1</u> (Dilute)	<u>Example 2</u> (Concentrate)
5	Cationic Softener (3)	4.7	12.7
	Coconut 20 EO Non-ionic	0.1	0.7
	Tallow Alcohol	--	0.7
	Silicone Anti-foam	0.03	0.015
	Cetyl hydroxyethyl cellulose	0.03	--
10	Proxel (4)	0.16	0.15
	Pearlescer (mica)	0.1	0.18
	Dye	0.0015	0.0048
	Perfume	0.32	0.95
-----			
15	(Emulsifier)	(1.67)	(5.0)
	Silicone PDMS	1.0	3.0
	COCOTMAMS	0.058	0.17
	COCOPEMAMS	0.032	0.1
-----			
20	Water, other preservatives	to 100	to 100

(3) Mixture of 1,2 bis[hardened tallowoxy]-3-trimethyl ammonium propane chloride and free fatty acid in a weight ratio of 6:1.

25 (4) Preservative

Example 3 (Performance Evaluation)

Compositions comprising by weight 12.7% of the cationic  
5 softener of Examples 1 and 2, 0.7% coconut 20 EO nonionic,  
0.7% tallow alcohol and 3% polydimethyl-siloxane (% active)  
obtained from different emulsions containing nonionic  
emulsifier and 50% by weight of the silicone active  
ingredient. To evaluate the first and third aspects of the  
10 present invention, the viscosity and median droplet sizes  
were varied between these different emulsions.

The nonionic-emulsified silicone emulsion was type HV600,  
available ex Dow Corning, but with the silicone viscosity  
15 and median droplet size being varied by the supplier, the  
other components being per the standard commercial product.

These formulations were evaluated in the rinse cycle as  
follows:-  
20

White cotton shirts were washed 4 times at 60°C to remove  
any pre-existing treatments which would distort the results.

25 Wash/rinse/dry cycles were then carried out. The conditions  
were as follows:

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Machine: Candy Aquaviva 1000  
Temperature: 40 °C  
Programme: Programme 5 - Non-fast coloureds recommended for cotton  
5 Water hardness: 13 °FH (Wirral water)  
Main wash product: 150g Persil Bio powder via shuttle  
Rinse products: 35 gm of a control composition containing 3% PDMS with a viscosity of 60,000cSt before emulsification OR 35 gm of a test composition containing 3% PDMS with viscosities before emulsification in the range 1,000cSt to 750,000cSt  
10 Washload: 10 shirts  
Drying: Hung on rails indoors  
15

2 extra shirts were added to the washes so that extraction could be carried out and silicone deposition estimated.  
20 These were split evenly over the washes.

Desized cotton poplin monitors were included for each product; 3 X 20cm by 20cm and 3 X 50cm by 100cm desized cotton poplin monitors were also included for measurement of 25 fabric physical properties.

The garments were assessed for:

1. Degree of creasing before ironing
2. Ease of ironing, Using steam

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The degree of creasing was assessed by paired comparisons between garments rinsed in the test and control products respectively. The garments were placed in the viewing cabinet and the assessor was asked Which is the least creased? . For the ease of ironing comparison, the panellist ironed two shirts using steam and was asked Which is the easiest to iron? . The irons used were Philips Azur 50 set at the temperature for cotton. 100ml of water was added for each panellist. The steam was set at maximum. Separate irons were used for each treatment to avoid possible transfer of rinse conditioner or silicone via the plate of the iron. The irons were washed and swapped halfway through the exercise to compensate for differences in the irons. Identical ironing boards were used.

The result obtained are summarised in the following table:-

- 20 -

Emulsion Characteristics		Degree of creasing (sample size 40)		Ease of ironing (sample size 20)	
Silicone Viscosity	Median Droplet Diameter (cSt)      ( $\mu\text{m}$ )	Score	Score (as %)	Score	Score (as %)
(a)	1,000      0.5	14	35.0	8	40
(b)	60,000      0.5	20	50.0	10	50
(c)	60,000      5.0	20	50.0	9	45
(d)	60,000      10.0	18	45.0	7	35
(e)	143,000      0.5	26	65.0	8	40
(f)	600,000      5.0	23	57.5	10	50
(g)	750,000      0.5	27	67.5	12	60
(h)	600,000      7.8	22	55.0	7	35

Sample (a) does not correspond to the invention, the viscosity being within the prior art range. All of samples 5 (b) - (h) showed a marked improvement in degree of creasing over sample (a). All except (d), (e) and (h) showed a marked improvement over (a) in terms of ease of ironing.

Example 4 (Performance Evaluation)

5 To evaluate the second and fourth aspects of the present invention, a comparison of effects on silicone deposition and performance in anti-creasing and anti-ironing was performed using a base fabric conditioner formulation as control:-

10	<u>Component</u>	<u>wt %</u>
	Cationic Softener(5)	4.8
	Nonionic 20 EO	0.1
	Tallow Alcohol	0.6

15 (5) Di-ethoxy ester (tallow)-di-methylammonium chloride

20 To the control formulation was added a PDMS emulsion at an amount equivalent to 1% silicone based on the weight of the softener composition, the balance being water (with minor ingredients), the viscosity of the silicone being 60,000cSt with a median droplet diameter of 0.5 $\mu\text{m}$  and emulsified, either with cationic or nonionic surfactants:-

	<u>Cationic System</u>	<u>Nonionic System</u>
25	Cetyl trimethyl ammoniumchloride (4.35%) + COCOPEMANS (1%)	HV600 (ex Dow Corning)

30 The weights in the cationic system are expressed as % by weight of the emulsion. The HV600 product is the nonionic-emulsified silicone referred to in Example 3.

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The products were dosed at 110ml to a washing machine rinse cycle and both shirts and T-shirts were evaluated for anti-creasing and ease of ironing. The cationic and nonionic 5 products were compared as a % of the control (i.e. minus silicone). Silicone deposition was evaluated by a standard method. The results obtained were as follows:-

Emulsi- fier System	T-Shirts Anti- crease Benefit %	Shirts Anti- crease Benefit %	T-Shirts Ironing Benefit %	Shirts Ironing Benefit %	T-Shirts Silicone Deposi- tion %	Shirts Silicone Deposi- tion %
Non- ionic	35	53	75	62	47	79
Cat- ionic	57	80	85	70	86	98

10

In all cases, the cationic emulsion shows a marked improvement in silicone deposition, anti-creasing and ease of ironing.

CLAIMS

1. A fabric softening composition comprising:-
  - (a) a cationic fabric softening agent; and
  - 5 (b) an emulsified silicone;wherein the viscosity of the silicone before emulsification is from 10,000cSt to 1,000,000cSt, preferably from 30,000cSt to 750,000cSt, more preferably from 40,000cSt to 400,000cSt, most preferably 45,000cSt to 250,000cSt, eg 45,000cSt to 10 200,000cSt and the emulsion is a macro-emulsion.
2. A composition according to claim 1, wherein, in the emulsified silicone, the median droplet size is from 0.39 $\mu\text{m}$  to 25 $\mu\text{m}$ .  
15
3. A composition according to either preceding claim, wherein the silicone is emulsified with an emulsifier comprising from one or more cationic surfactants, preferably having a non-halogen counter-ion and/or selected from alkyl 20 tri-methylammonium methosulphates and derivatives in which at least two of the methyl groups on the nitrogen atom are replaced by (poly) alkoxylated groups.
4. A fabric softening composition comprising:-
  - 25 (a) a cationic fabric softening agent; and
  - (b) an emulsified silicone;wherein the median droplet size of the silicone in the emulsion is at least 0.2 $\mu\text{m}$ , preferably at least 0.25 $\mu\text{m}$ , more preferably at least 0.39 $\mu\text{m}$ , preferably also no greater than 30 25 $\mu\text{m}$  and is emulsified with an emulsifier comprising one or more cationic surfactants.

5. A composition according to claim 4, wherein the viscosity of the silicone before emulsification is from 10,000cSt to 1,000,000cSt, preferably from 30,000cSt to 5 750,000cSt, more preferably from 40,000cSt to 400,000cSt, most preferably 45,000cSt to 250,000cSt, eg 45,000 to 200,000cSt.
10. 6. A composition according to claim 4 or claim 5, in which the cationic surfactant(s) is/are selected from those having a non-halogen counter-ion and/or selected from those in which at least two of the methyl groups on the nitrogen atom are replaced by (poly)alkoxylated groups.
15. 7. A composition according to any preceding claim, wherein in the emulsion, the total amount of emulsifying surfactant is from 0.5% to 20%, preferably from 2% to 12%, more preferably from 3% to 10%, by weight of the total composition, the weight ratio of silicone to total 20 emulsifying surfactant, preferably being from 3:1 to 120:1, more preferably from 3:1 to 120:1.
25. 8. A composition according to any preceding claim, wherein the cationic fabric softening agent is selected from quaternary ammonium and ester-linked quaternary ammonium compounds.
30. 9. A composition according to claim 8, wherein the cationic fabric softening agent is selected from 1,2 bis[hardened-tallowoxy]-3-trimethylammonium propane chloride, diethoxy ester(tallow)dimethyl ammoniumchloride,

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dihardened-tallow-dimethyl ammoniumchloride and di-(tallowyloxyethyl)methyl hydroxyethyl methosulphate, and mixtures thereof.

- 5 10. A composition according to any preceding claim, wherein the total amount of cationic fabric softening agent is from 0.5% to 35%, preferably from 1% to 30%, more preferably from 3% to 25% by weight of the total composition.
- 10 11. A composition according to any preceding claim, wherein the silicone is a poly-di-C<sub>1</sub>-6alkylsiloxane (preferably polydimethylsiloxane) end-terminated by tri-C<sub>1</sub>-6alkylsilyl (preferably trimethylsilyl) groups or by hydroxy-di-C<sub>1</sub>-6 alkylsilyl (preferably hydroxy-dimethylsilyl) groups or a 15 mixture of both.
12. A composition according to any preceding claim, wherein the weight ratio of total fabric softening agent to total silicone is from 1:1 to 70:1, preferably from 1.5:1 to 25:1.
- 20 13. A method of manufacturing a composition according to any preceding claim, the method comprising obtaining the emulsion in the form a macro-emulsion of a silicone having a viscosity of from 10,000cSt to 1,000,000cSt and admixing it 25 with the cationic fabric softening agent, and optionally with any other component(s).
14. A method of manufacturing a fabric softening composition according to any of claims 1-12, the method comprising obtaining the emulsion in the form of an emulsion
- 30

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of a silicone having a viscosity of from 10,000cSt to 1,000,000cSt, preferably from 30,000cSt to 750,000cSt, more preferably from 40,000cSt to 400,000cSt, most preferably 45,000cSt to 250,000cSt, eg 45,000cSt to 200,000cSt, the 5 median droplet size of the silicone in the emulsion being at least 0.2 $\mu$ m, preferably at least 0.25 $\mu$ m, more preferably at least 0.39 $\mu$ m, preferably also no greater than 25 $\mu$ m and is emulsified with an emulsifier comprising one or more cationic surfactants, and admixing said emulsion with the 10 cationic fabric softening agent, and optionally with any other component(s).

15. A method of softening a fabric, the method comprising applying to that fabric, a composition according to any of 15 claims 1-12.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/04223

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7	D06M15/643	D06M13/463	C11D3/37	C11D1/62	C11D17/00
C11D3/00					

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7	D06M	C11D		
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>WO 97 31998 A (PROCTER &amp; GAMBLE)          4 September 1997 (1997-09-04)          cited in the application          page 4, line 7 - line 19          page 6, line 1 -page 7, line 23          examples          claims 1-3,9-12</p> <p>---</p>	4,6-8, 10-12,15
X	<p>EP 0 285 391 A (TORAY SILICONE CO)          5 October 1988 (1988-10-05)          page 2, line 52 -page 3, line 6          page 3, line 25 - line 26          examples 2,5</p> <p>---</p> <p>---</p>	1-8, 10-15

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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**INTERNATIONAL SEARCH REPORT**

International Application No

PCT/EP 00/04223

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

International Application No

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WO 01/25386 A1

(54) Title: FABRIC CARE COMPOSITION

(57) Abstract: Fabric care compositions adapted for use in a laundering process such as detergent compositions and laundry rinse compositions, comprise at least one reactive cationic polymer (preferably amine- or amide-epichlorohydrin resin or a derivative thereof), at least one reactive anionic polymer and at least one textile compatible carrier. The compositions have improved dye transfer and stain release properties and may be used in methods of treating fabric as part of a laundering process.

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### FABRIC CARE COMPOSITION

#### Technical Field

5 This invention relates to fabric care compositions, including detergent compositions and laundry rinse compositions. The invention also relates to methods of treating fabric using the compositions of the invention and to the use of anionic polymers in fabric care compositions.

10

#### Background and Prior Art

The laundry process generally has several benefits for fabric, the most common being to remove dirt and stains from 15 the fabric during the wash cycle and to soften the fabric during the rinse cycle. However, there are numerous disadvantages associated with repeated use of conventional laundry treatment compositions and/or the actual laundry process; one of these being a fairly harsh treatment of 20 fabric in the laundry process.

Fabrics can be damaged in several ways as a result of repeated laundering and/or wear. Fabric pilling and loss of fabric surface appearance eg fuzzing, shrinkage (or 25 expansion), loss of colour from the fabric or running of colour on the fabric (usually termed dye transfer) are some of the common problems associated with repeated laundering. These problems may occur merely from repeated hand washing as well as the more vigorous machine washing process. 30 Furthermore, problems relating to damage of fabric over time through normal use, such as loss of shape and increased

- 2 -

likelihood of wrinkling are also significant, especially with articles of clothing.

Laundry detergent compositions containing polyamide-  
5 polyamine fabric treatment agents are described in WO  
98/29530. The compositions are claimed to impart improved  
overall appearance to fabrics laundered using the detergent  
compositions, in terms of surface appearance properties such  
as pill/fuzz reduction and antifading. Laundry compositions  
10 containing polyamide-polyamine treatment agents of similar  
types are taught in WO 97/42287.

An industrial process for treating fibres is disclosed in US  
3949014. This document describes the use of a polyamine-  
15 epichlorohydrin resin in a binder, together with an  
amphoteric high molecular weight compound having at least 2  
cationic groups and at least 2 anionic groups per molecule.  
US 3949014 mentions the treatment of fabrics with the binder  
but it is clear that the treatment is intended to be carried  
20 out industrially as part of a fabric treatment process  
rather than as part of a domestic laundering process and  
this conclusion is supported by the fact that the fabric  
treated with the binder required curing at a relatively high  
temperature. Industrial curing of fabrics treated with this  
25 type of polymer is normally carried out at about 150°C.

Methods for treating wool with compositions containing an  
amino functional polymer and a silicone polymer so as to  
impart shrink resistance are known. However, as described  
30 in EP-A-0315477, wool requires a pretreatment before such  
compositions can be used. Furthermore, EP-A-0372782

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explains that the chemistry of wool is quite different from that of cellulosic fibres such as cotton and the requirements for shrink resistance treatments for cotton are generally very different from those for wool.

5

US 4371517 discloses a composition for treating fibrous materials which contain cationic and anionic polymers. In a non-domestic treatment, the compositions increased the rigidity of cotton fabric.

10

Detergent compositions which prevent dye transfer are taught in EP-A-0068232. The compositions contain nonionic or zwitterionic surfactants in combination with water-soluble, amino and/or amide group-containing polymers.

15

WO 98/17764 discloses the use of polyamidoamines, in washing and cleaning compositions, as soil release agents.

20

Co-emulsifiers, for use in fabric softener and other compositions, which contain cationic quaternary amine polymers, are taught in DD 221922.

25

GB 2005322 discloses a method of treating textiles which involves treating the materials with a water-soluble polymeric material and an exhaustion agent. The polymers disclosed include the anionic polycarbamoyl-sulphonates. The exhaustion agents are inorganic salts.

30

US 4121902 discloses a textile treatment composition which comprise water-soluble anionic polymers (polycarbamoylsulphonates) and at least 20% of a water-

- 4 -

insoluble organic polymer. Optional ingredients which may be present include cationic derivatives of polyamides (such as epichlorohydrin derivatives) or cationic surfactants.

5 GB 1329247 discloses a process for rendering keratinous or other protein material resistant to shrinkage. The process comprises a treatment with a resin followed treatment with a soil release agent. The resin can be a cationic derivatives of polyamide (such as an epichlorohydrin derivative).

10 GB 2039938 discloses a textile treatment composition which includes both anionic and cationic polymers.

**Definition of the Invention**

15 According to the present invention, there is provided a fabric care composition adapted for use in a domestic laundering process and comprising:  
a) at least one reactive cationic polymer,  
20 b) at least one reactive anionic polymer, and,  
c) at least one textile compatible carrier,  
said reactive polymers each being capable of self cross-linking and/or cross linking to cellulose, wherein the cationic polymer and the anionic polymer are present in  
25 amounts such that the overall charge provided by the polymers is positive, and wherein the composition comprises less than 10% of water-insoluble organic polymers.

It is believed that the use of an anionic polymer improves  
30 the dye transfer properties of a fabric care composition which comprises a cationic polymer.

- 5 -

It is also believed that use of an anionic polymer improves the stain release properties of a fabric care composition which comprises a cationic polymer.

5

Also provided by the present invention is a method of treating fabric comprising applying to the fabric a fabric care composition according to the invention as part of a laundering process.

10

**Detailed Description of the Invention**

Preferably, the reactive cationic polymer is an amine- or amide-epichlorohydrin resin or derivative thereof.

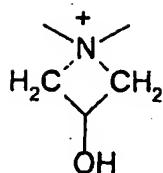
15. Preferably these cationic polymers have a weight average mean molecular weight of from 300 to 1,000,000 Dalton.

The preferred epichlorohydrin resins of the invention are sometimes referred to below as amine-epichlorohydrin resins 20 and polyamine-epichlorohydrin (PAE) resins (the two terms being used synonymously) although these terms encompass both the amine and amide resins of the invention and their derivatives. The resins may also have a mixture of amine and amide groups.

25

The amine- or amide-epichlorohydrin resins may have one or more functional groups capable of forming azetidinium groups and/or one or more azetidinium functional groups.

- 6 -



Alternatively, or additionally, the resins may have one or more functional groups that contain epoxide groups or derivatives thereof eg Kymene™ 450 (ex Hercules).

5

Suitable polyamine-epichlorohydrin (PAE) resins include those described in "Wet Strength Resins and Their Application", pp 16-36, ed. LL Chan, Tappi Press, Atlanta, 1994. Suitable resins can be identified by selecting those 10 resins which impart increased wet strength to paper, after treatment, in a relatively simple test.

Any amine- or amide-epichlorohydrin resin having an epoxide functional group or derivative thereof is suitable for use 15 according to the invention.

A particularly preferred class of amine- or amide-epichlorohydrin resins for use in the invention are secondary amine- or amide-based azetidinium resins, for 20 example those resins derived from a polyalkylene polyamine eg diethylenetriamine (DETA), a polycarboxylic acid eg adipic acid or other dicarboxylic acids, and epichlorohydrin. Other polyamines or polyamides can also be advantageously used in the preparation of suitable PAE 25 resins.

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Another preferred class of amine-epichlorohydrin resins for use in the invention are those having an epoxide functional group or derivative thereof eg a chlorohydrin group.

- 5 The resin is preferably present in the product in a sufficient quantity to give an amount of 0.0005-5% by weight on the fabric based on the weight of fabric (owf), more preferably 0.001-2% owf. The amount of the resin in the composition required to achieve the above % by weight on fabric will typically be in the range 0.01% to 35% by weight, preferably 0.1% to 13.5% by weight.
- 10

The resin may be a PDAA-epichlorohydrin resin or a PMDAA-epichlorohydrin resin. PDAA is poly(diallylamine) and PMDAA is poly(methyldiallyl (amine)).

The fabric care compositions of the invention also comprise at least one reactive anionic polymer.

- 20 The reactive anionic polymer is present in the composition in an amount such that the overall negative charge contributed by the anionic groups of the anionic polymer is less than the positive charge provided by the cationic groups of the cationic polymer (such as the amine-epichlorohydrin resin) and any cationic groups in the anionic polymer.
- 25

Suitable amounts of reactive anionic polymer in the composition are in the range of from 0.01% to 35% by weight, preferably 0.1% to 13.5% by weight. If the overall charge provided by the anionic polymer and the cationic polymer, as

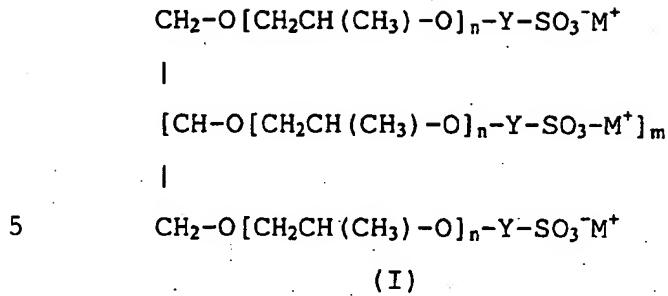
described above, is not positive, it is believed that the cationic polymer tends not to impart the benefits to the fabric which are imparted to the fabric in the absence of the anionic polymer.

5

The anionic polymer may be any polymeric compound having a single unit which repeats in the compound, on average at least five times, a plurality of anionic groups and a molecular weight of at least 400 Dalton, preferably at least 10 600 Dalton. The anionic polymer has negatively charged groups which may be present in the repeating group and/or at one or both of the ends of the polymer chain and may be introduced during polymerisation or after the polymer has been formed. The anionic polymer may contain cationic 15 groups as well as anionic groups but the net charge on the polymer chain must be negative. The anionic polymer can be wholly or partly amphoteric, provided that it is capable of having a net negative charge in the presence of the cationic polymer. It is preferred that the anionic polymer comprises 20 anionic groups which are oxo-anions of sulphur, carbon or phosphorus, or derivatives thereof such as, for example, sulphonate ( $\text{SO}_3^-$ ) and carboxylate ( $\text{CO}_2^-$ ) groups.

Preferred anionic polymers are polyisocyanate derivatives, 25 preferably the bisulphite addition products such as polycarbamoyl sulphamates. Preferably, the anionic polymer is selected from carbamoyl sulphonate terminated poly(ether)urethane resins, bunte salt terminated polymers and mixtures thereof. Suitable polymers include those 30 having the formula (I):

- 9 -



wherein:

- 10 Y is a divalent radical selected from  $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{S}-$  and  $-\text{CO}-\text{NH}-\text{(CH}_2\text{)}_p-\text{NH}-\text{CO}-$ ;
- m is an integer from 0 to 4;
- n is an integer from 5 to 20;
- M is an alkali metal; and
- 15 p is an integer from 2 to 12.

Preferably, m is equal to 1.

Conveniently, Y is  $-\text{CO}-\text{NH}-\text{(CH}_2\text{)}_p-\text{NH}-\text{CO}-$

- 20 and, preferably, p is from 4 to 8, such as about 6.

It is also preferred that n is 10 to 15, such as about 13, for example.

- 25 M is advantageously sodium or potassium, more preferably sodium.

Polymers in which Y is  $-\text{CO}-\text{NH}-\text{(CH}_2\text{)}_p-\text{NH}-\text{CO}-$  are commercially available under the Trade Mark SYNTHAPPRET BAP (Bayer).

- 10 -

Polymers in which Y is  $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{S}-$  are available under the Trade Mark NOPCOLAN SHR3 (Henkel).

The compositions of the invention, when applied to a fabric,  
5 may be cured by a domestic curing step including ironing and/or domestic tumble drying, preferably tumble drying. Preferably, these curing steps are carried out at temperatures in the range of from 60 to 100°C, more preferably from 80 to 100°C.

10 The compositions of the invention may be used before, during or after a conventional laundry process and are preferably packaged and labelled as such. The laundry process includes large and small scale processes, and is preferably a  
15 domestic process.

When the compositions of the invention are to be used before or after the laundry process, they may be in the form of a spray or foaming product.

20 When the compositions of the invention are to be used during the laundry process, they may be used at any convenient stage of the process, such as, for example, in a pre-wash composition, in the main wash detergent composition and/or a  
25 rinse composition.

In the context of the present invention the term 'textile compatible carrier' means a component which can assist in the interaction of the cationic polymer with the fabric.  
30 The carrier can also provide benefits in addition to those provided by the cationic polymer e.g. softening, cleaning

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etc. The nature of the carrier will depend upon at what stage of the laundry process the composition of the invention is used. The carrier may be water or a detergent-active compound or a fabric softener or conditioning 5 compound or other suitable detergent or fabric treatment agent.

If the composition of the invention is to be used in a laundry process as part of a conventional fabric treatment 10 product, such as a detergent composition, the textile-compatible carrier will typically be a detergent-active compound. Whereas, if the fabric treatment product is a rinse conditioner, the textile-compatible carrier will be a fabric softening and/or conditioning compound.

15

#### **Detergent Active Compounds**

If the composition of the present invention is in the form of a detergent composition (such as a main wash 20 composition), the textile-compatible carrier may be chosen from soap and non-soap anionic, cationic, nonionic, amphoteric and zwitterionic detergent active compounds, and mixtures thereof.

25 Many suitable detergent active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

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The preferred textile-compatible carriers that can be used are soaps and synthetic non-soap anionic and nonionic compounds.

- 5 Anionic surfactants are well-known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C<sub>8</sub>-C<sub>15</sub>; primary and secondary alkyl sulphates, particularly C<sub>8</sub>-C<sub>15</sub> primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.
- 10

Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C<sub>8</sub>-C<sub>20</sub> aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C<sub>10</sub>-C<sub>15</sub> primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

Cationic surfactants that may be used include quaternary ammonium salts of the general formula R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub>N<sup>+</sup> X<sup>-</sup> wherein the R groups are independently hydrocarbyl chains of C<sub>1</sub>-C<sub>22</sub> length, typically alkyl, hydroxyalkyl or ethoxylated alkyl groups, and X is a solubilising anion (for example, compounds in which R<sub>1</sub> is a C<sub>8</sub>-C<sub>22</sub> alkyl group, preferably a C<sub>8</sub>-C<sub>10</sub> or C<sub>12</sub>-C<sub>14</sub> alkyl group, R<sub>2</sub> is a methyl group, and R<sub>3</sub> and

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$R_4$ , which may be the same or different, are methyl or hydroxyethyl groups); and cationic esters (for example, choline esters) and pyridinium salts.

5 The total quantity of detergent surfactant in the composition is suitably from 0.1 to 60 wt%, eg 0.5-55 wt%, such as 5-50 wt%.

Preferably, the quantity of anionic surfactant (when present) is in the range of from 1 to 50% by weight of the total composition. More preferably, the quantity of anionic surfactant is in the range of from 3 to 55% by weight, eg 5 to 30% by weight.

15 Preferably, the quantity of anionic surfactant is in the range of from 3 to 35% by weight, eg 5 to 30% by weight.

Preferably, the quantity of nonionic surfactant when present is in the range of from 2 to 25% by weight, more preferably from 5 to 20% by weight.

Amphoteric surfactants may also be used, for example amine oxides or betaines.

25 The compositions may suitably contain from 10 to 70%, preferably from 15 to 70% by weight, of detergency builder. Preferably, the quantity of builder is in the range of from 15 to 50% by weight.

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The detergent composition may contain as builder a crystalline aluminosilicate, preferably an alkali metal aluminosilicate, more preferably a sodium aluminosilicate.

5 The aluminosilicate may generally be incorporated in amounts of from 10 to 70% by weight (anhydrous basis), preferably from 25 to 50%. Aluminosilicates are materials having the general formula:

10  $0.8-1.5 \text{ M}_2\text{O} \text{ Al}_2\text{O}_3 \cdot 0.8-6 \text{ SiO}_2$

where M is a monovalent cation, preferably sodium. These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g.

15 The preferred sodium aluminosilicates contain 1.5-3.5 SiO<sub>2</sub> units in the formula above. They can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature.

20 **Fabric Softening and/or Conditioner Compounds**

The compositions of the invention may be in the form of a rinse composition, such as a fabric conditioner composition.

25 Therefore, also provided by the present invention are laundry rinse compositions comprising at least one reactive cationic (preferably amine- or amide-epichlorohydrin) resin, at least one reactive anionic polymer and at least one textile compatible carrier. The laundry rinse compositions  
30 may contain an anionic surfactant which may be one or more of the anionic surfactants which may be used in the

- 15 -

detergent active compositions described above. The rinse compositions may contain both an anionic polymer and an anionic surfactant and contain an amount of anionic polymer and/or anionic surfactant which provides a total negative 5 charge from its anionic groups that is not greater than the total positive charge provided by the cationic groups of the amine-epichlorohydrin resin and any cationic groups in the anionic polymer. Suitable amounts of both the cationic (preferably amine-epichlorohydrin) resin and the total 10 anionic polymer and/or anionic surfactant are in the range of from 0.01 to 35% by weight, (preferably 0.1% to 13.5% by weight, more preferably 3 to 7% by weight) so as to provide an amount of the components on the fabric of from 0.0005 to 5% by weight of the fabric, preferably 0.001 to 2% by weight 15 of the fabric.

If the fabric care composition or the laundry rinse composition of the present invention is in the form of a fabric conditioner composition, the textile-compatible 20 carrier will be a fabric softening and/or conditioning compound (hereinafter referred to as "fabric softening compound"), which may be a cationic or nonionic compound.

The softening and/or conditioning compounds may be water 25 insoluble, non-polymeric, quaternary ammonium compounds. The compounds may be present in amounts of up to 8% by weight (based on the total amount of the composition) in which case the compositions are considered dilute, or at levels from 8% to about 50% by weight, in which case the 30 compositions are considered concentrates.

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Compositions suitable for delivery during the rinse cycle may also be delivered to the fabric in the tumble dryer if used in a suitable form. Thus, another product form is a composition (for example, a paste) suitable for coating 5 onto, and delivery from, a substrate eg a flexible sheet or sponge or a suitable dispenser (such as a container having apertures therein, for example) during a tumble dryer cycle.

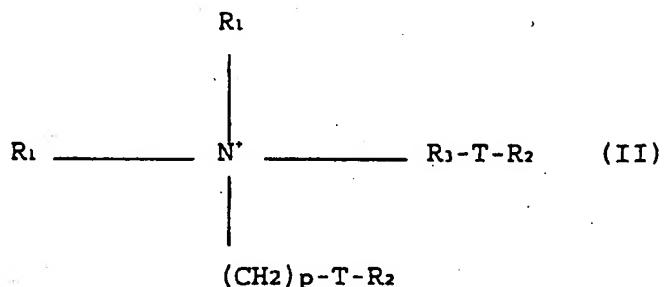
Suitable cationic fabric softening compounds are 10 substantially water-insoluble quaternary ammonium materials comprising a single alkyl or alkenyl long chain having an average chain length greater than or equal to C<sub>20</sub> or, more preferably, compounds comprising a polar head group and two alkyl or alkenyl chains having an average chain length 15 greater than or equal to C<sub>14</sub>. Preferably the fabric softening compounds have two long chain alkyl or alkenyl chains each having an average chain length greater than or equal to C<sub>16</sub>. Most preferably at least 50% of the long chain alkyl or alkenyl groups have a chain length of C<sub>18</sub> or above. 20 It is preferred if the long chain alkyl or alkenyl groups of the fabric softening compound are predominantly linear.

Quaternary ammonium compounds having two long-chain aliphatic groups, for example distearyldimethyl ammonium 25 chloride and di (hardened tallow alkyl) dimethyl ammonium chloride, are widely used in commercially available rinse conditioner compositions. Other examples of these cationic compounds are to be found in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch. 30 Any of the conventional types of such compounds may be used in the compositions of the present invention.

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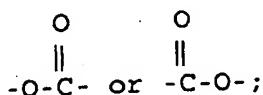
The fabric softening compounds are preferably compounds that provide excellent softening, and are characterised by a chain melting  $L\beta$  to  $L\alpha$  transition temperature greater than 5  $25^{\circ}\text{C}$ , preferably greater than  $35^{\circ}\text{C}$ , most preferably greater than  $45^{\circ}\text{C}$ . This  $L\beta$  to  $L\alpha$  transition can be measured by DSC as defined in "Handbook of Lipid Bilayers", D Marsh, CRC Press, Boca Raton, Florida, 1990 (pages 137 and 337). Substantially water-insoluble fabric softening compounds are 10 defined as fabric softening compounds having a solubility of less than  $1 \times 10^{-3}$  wt % in demineralised water at  $20^{\circ}\text{C}$ . Preferably the fabric softening compounds have a solubility of less than  $1 \times 10^{-4}$  wt %, more preferably less than  $1 \times 10^{-8}$  to  $1 \times 10^{-6}$  wt %.

15 Especially preferred are cationic fabric softening compounds that are water-insoluble quaternary ammonium materials having two  $C_{12-22}$  alkyl or alkenyl groups connected to the molecule via at least one ester link, preferably two ester 20 links. An especially preferred ester-linked quaternary ammonium material can be represented by the formula II:



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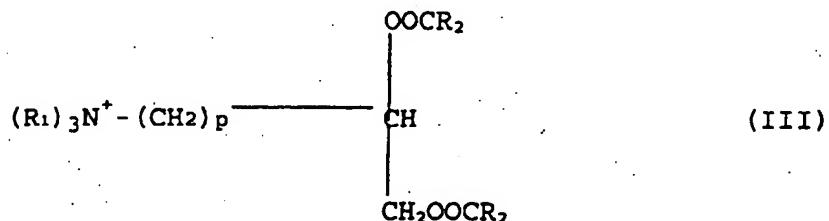
wherein each  $R_1$  group is independently selected from  $C_{1-4}$  alkyl or hydroxyalkyl groups or  $C_{2-4}$  alkenyl groups; each  $R_2$  group is independently selected from  $C_{8-28}$  alkyl or alkenyl groups; and wherein  $-R_3-$  is a linear or branched alkylene group of 1 to 5 carbon atoms, T is



and p is 0 or is an integer from 1 to 5.

10 Di (tallowoyloxyethyl) dimethyl ammonium chloride and/or its hardened tallow analogue is especially preferred of the compounds of formula (II).

15 A second preferred type of quaternary ammonium material can be represented by the formula (III):



wherein  $R_1$ , p and  $R_2$  are as defined above.

It is advantageous if the quaternary ammonium material is  
20 biologically biodegradable.

- 19 -

Preferred materials of this class such as 1,2-bis (hardened tallowoyloxy) -3-trimethylammonium propane chloride and their methods of preparation are, for example, described in US 4 137 180 (Lever Brothers Co). Preferably these

5 materials comprise small amounts of the corresponding monoester as described in US 4 137 180, for example, 1-hardened tallowoyloxy-2-hydroxy-3-trimethylammonium propane chloride.

10 Other useful cationic softening agents are alkyl pyridinium salts and substituted imidazoline species. Also useful are primary, secondary and tertiary amines and the condensation products of fatty acids with alkylpolyamines.

15 The compositions may alternatively or additionally contain water-soluble cationic fabric softeners, as described in GB 2 039 556B (Unilever).

20 The compositions may comprise a cationic fabric softening compound and an oil, for example as disclosed in EP-A-0829531.

25 The compositions may alternatively or additionally contain nonionic fabric softening agents such as lanolin and derivatives thereof.

Lecithins are also suitable softening compounds.

30 Nonionic softeners include L $\beta$  phase forming sugar esters (as described in M Hato et al Langmuir 12, 1659, 1966, (1996)) and related materials such as glycerol monostearate

- 20 -

or sorbitan esters. Often these materials are used in conjunction with cationic materials to assist deposition (see, for example, GB 2 202 244). Silicones are used in a similar way as a co-softener with a cationic softener in 5. rinse treatments (see, for example, GB 1 549 180).

The compositions may also suitably contain a nonionic stabilising agent. Suitable nonionic stabilising agents are linear C<sub>8</sub> to C<sub>22</sub> alcohols alkoxylated with 10 to 20 moles of 10 alkylene oxide, C<sub>10</sub> to C<sub>20</sub> alcohols, or mixtures thereof. Advantageously the nonionic stabilising agent is a linear C<sub>8</sub> to C<sub>22</sub> alcohol alkoxylated with 10 to 20 moles of alkylene oxide. Preferably, the level of nonionic stabiliser is within the range from 0.1 to 10% by weight, more preferably 15 from 0.5 to 5% by weight, most preferably from 1 to 4% by weight. The mole ratio of the quaternary ammonium compound and/or other cationic softening agent to the nonionic stabilising agent is suitably within the range from 40:1 to about 1:1, preferably within the range from 18:1 to about 20 3:1.

The composition can also contain fatty acids, for example C<sub>8</sub> to C<sub>24</sub> alkyl or alkenyl monocarboxylic acids or polymers thereof. Preferably saturated fatty acids are used, in 25 particular hardened tallow C<sub>16</sub> to C<sub>18</sub> fatty acids. Preferably the fatty acid is non-saponified, more preferably the fatty acid is free, for example oleic acid, lauric acid or tallow fatty acid. The level of fatty acid material is preferably more than 0.1% by weight, more preferably more than 0.2% by 30 weight. Concentrated compositions may comprise from 0.5 to

- 21 -

20% by weight of fatty acid, more preferably 1% to 10% by weight. The weight ratio of quaternary ammonium material or other cationic softening agent to fatty acid material is preferably from 10:1 to 1:10.

5

The fabric conditioning compositions may include silicones, such as predominantly linear polydialkylsiloxanes, eg polydimethylsiloxanes or aminosilicones containing amine-functionalised side chains; soil release polymers such as 10 block copolymers of polyethylene oxide and terephthalate; amphoteric surfactants; smectite type inorganic clays; zwitterionic quaternary ammonium compounds; and nonionic surfactants. Preferably, the silicone component is a dimethylpolysiloxane with aminoalkyl groups.

15

The fabric conditioning compositions may also include an agent which produces a pearlescent appearance, eg an organic pearlising compound such as ethylene glycol distearate, or inorganic pearlising pigments such as microfine mica or 20 titanium dioxide ( $TiO_2$ ) coated mica.

The fabric conditioning compositions may be in the form of emulsions or emulsion precursors thereof.

25

Other optional ingredients include emulsifiers, electrolytes (for example, sodium chloride or calcium chloride) preferably in the range from 0.01 to 5% by weight, pH buffering agents, and perfumes (preferably from 0.1 to 5% by weight).

30

- 22 -

Further optional ingredients include non-aqueous solvents, perfume carriers, fluorescers, colourants, hydrotropes, antifoaming agents, antiredeposition agents, enzymes, optical brightening agents, opacifiers, anti-shrinking agents, anti-wrinkle agents, anti-spotting agents, dye transfer inhibitors, germicides, fungicides, anti-oxidants, UV absorbers (sunscreens), heavy metal sequestrants, chlorine scavengers, dye fixatives, anti-corrosion agents, drape imparting agents, antistatic agents and ironing aids.

5      This list is not intended to be exhaustive.

10

#### **Fabric Treatment Products**

The composition of the invention may be in the form of a liquid, solid (eg powder or tablet), a gel or paste, spray, stick or a foam or mousse. Examples include a soaking product, a rinse treatment (eg conditioner or finisher) or a mainwash product. The composition may also be applied to a substrate (eg a flexible sheet) or used in a dispenser which can be used in the wash cycle, rinse cycle or during the dryer cycle.

15

20

The fabric care compositions of the present invention have been found to possess the advantages of compositions containing cationic amine-epichlorohydrin resins, such as improved surface colour definition of the fabric following multiple washings and/or improved dimensional stability of the fabric and/or reduced fabric fibrillation. Moreover, the compositions of the invention exhibit reduced dye transfer and/or improved stain release properties relative to those compositions.

25

30

The use of anionic polymers to improve the dye transfer properties of a fabric care composition and/or to improve the stain release properties of a fabric care composition is 5 applicable to compositions containing amine-epichlorohydrin resins and/or other cationic polymers. Fabrics treated with the compositions of the invention can also exhibit beneficial properties due to the anionic polymer itself, such as antistatic properties, for example.

10 The fabrics which may be treated in the present invention may be in the form of garments and preferably comprise cellulosic fibres, preferably from 1% to 100% cellulosic fibres (more preferably 5% to 100% cellulosic fibres, most 15 preferably 40% to 100% such as 75% to 100%). When the fabric contains less than 100% cellulosic fibres, the balance comprises other fibres or blends of fibres suitable for use in garments such as polyester or polyamide, for example. Preferably, the cellulosic fibres are of cotton or 20 regenerated cellulose such as viscose.

The invention will now be described by way of example only and with reference to the following non-limiting examples.

25 EXAMPLES 1 TO 2

Fabric Preparation

30 All samples were prepared by repeating the following method five times:

- 24 -

730g of fabric (3 pieces undyed woven cotton sheeting, 1 piece of printed fabric for fabric care evaluation) was washed at 40°C on a cotton wash cycle with 35g of Persil Original Non-Biological (trade mark) detergent. Samples were 5 treated by rinse applying the required amount of product in the rinse cycle.

The products applied were:

10 Control - 0.1% Apomul SAK™ (polyamine-epichlorohydrin resin, as about 13% aqueous solution, Brookstone Chemicals)  
Example 1 - 0.1% Apomul SAK™ + 0.1% Synthappret BAP™  
Example 2 - 0.1% Apomul SAK™ + 0.15% Synthappret BAP™

15 Synthappret BAP™ is a polycarbamoyl sulphonate (a bisulphite adduct of a polyisocyanate).

After the five applications, samples of each treatment were evaluated for dye transfer and stain release.

20

Dye transfer

30 cm square samples of the control and the product treated according to the invention were washed at 40°C on a cotton wash cycle in a Zanussi Jetsystem 1200 (trade mark) washing machine with 35g of Persil Original Non-Biological (trade mark) detergent together with Direct Red 80 standard cloths at a ratio of 6:1 treated : Direct Red 80 followed by tumble drying in a Miele Novotronic T430 (trade mark) tumble dryer 25 30 on "extra dry" setting. The change in colour ( $\Delta E$ ) of the

- 25 -

treated fabrics relative to untreated cloth subjected to the same dye transfer test was then measured using the Spectraflash (trade mark) spectrometer.

5. Treatment                    ΔE

Control	8.12
Example 1	4.92
Example 2	4.49

10

Stain Release

Samples of the treated fabrics had 1 ml of red wine applied to the centre of the sample. After the wine had soaked in, 15 the sample was left under ambient conditions for five days. The stained area was then measured using the Spectraflash (trade mark) spectrometer. The samples were then washed at 40°C with 35g of Persil Biological Powder (trade mark), tumble dried and the stains measured again.

20

	<u>Treatment</u>	<u>ΔE of stain</u>	<u>ΔE after washing</u>	<u>ΔΔE</u>
	Control	25.36	11.82	13.54
	Example 1	25.82	12.15	13.67
25	Example 2	25.39	10.28	15.11

In this case the larger ΔΔE value, the more stain has been removed (ie the colour is paler).

30

Garment Care Benefits

The method used to determine the garment care benefit from the cationic polymers involved the determination of the 5 effect of washing treatment on the colour and lightness of a printed fabric which is particularly susceptible to surface damage which appears as a change in the colour of the print.

The load used for the experiment consisted of three pieces 10 of woven cotton sheeting 1m x 1.52m weighing approximately 700 g in total, and a piece of the printed fabric measuring 0.5m x 1m weighing approximately 30g, giving a total load weight of 730g. This allows the fabric freedom to move within the machine resulting in more damage.

15 The wash was carried out in a Zanussi Jetsystem 1200 (trade mark) washing machine at 40°C using 35g of Persil Original Non-Biological (trade mark) washing powder in the main wash. Treatments were applied in the rinse at a level to deliver 20 0.2% o.w.f of active ingredient.

After each cycle, the load was tumble dried in a Miele Novotronic T430 (trade mark) dryer using the extra-dry setting.

25 After five wash/dry cycles, the appearance was compared to an untreated sample and colour measurements were taken as necessary.

30 Where colour measurements were taken, the greater the change in colour ( $\Delta E$ ) or lightness ( $\Delta L$ ) indicates more severe

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damage which causes the colour to change more dramatically. The smaller the  $\Delta E$  and  $\Delta L$  values, the closer the fabric appearance is to the original, indicating a positive garment care benefit.

5

Colour measurements were carried out on areas of the printed fabric which had been dyed black and red. The results are as follows:

10 i. Black

Treatment	$\Delta L$	$\Delta E$
None	9.94	10.07
0.1% Apomul SAK™	4.15	4.25
0.2% Apomul SAK™	4.29	4.57
0.2% Synthappret BAP™	8.66	8.72
Example 1	2.46	2.61
Example 2	2.77	2.82

ii. Red

Treatment	$\Delta L$	$\Delta E$
None	3.30	12.62
0.1% Apomul SAK™	0.91	6.11
0.2% Apomul SAK™	0.71	5.85
0.2% Synthappret BAP™	2.79	11.24
Example 1	0.43	5.56
Example 2	0.66	5.04

15 The results for the red and black areas of the printed fabric show that, in both cases, the colour care benefits of the cationic polymers are not only maintained but are surprisingly improved upon by the cationic/anionic polymer compositions of the invention.

CLAIMS

1. Fabric care composition adapted for use in a domestic laundering process and comprising:
  - 5 a) at least one reactive cationic polymer,
  - b) at least one reactive anionic polymer, and,
  - c) at least one textile compatible carrier,  
said reactive polymers each being capable of self cross-linking and/or cross linking to cellulose, wherein the
  - 10 cationic polymer and the anionic polymer are present in amounts such that the overall charge provided by the polymers is positive, and wherein the composition comprises less than 10% of water-insoluble organic polymers.
- 15 2. Composition as claimed in Claim 1, wherein the reactive cationic polymer is an amine- or amide-epichlorohydrin resin and is present in the composition in an amount of from 0.01 to 35% by weight.
- 20 3. Composition as claimed in Claim 1 wherein the reactive anionic polymer is present in the composition in an amount of from 0.01 to 35% by weight.
- 25 4. Composition as claimed in Claim 2, wherein the amine- or amide-epichlorohydrin resin has one or more functional groups capable of forming azetidinium groups.
- 30 5. Composition as claimed in Claim 2, wherein the amine- or amide-epichlorohydrin resin has one or more azetidinium groups.

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6. Composition as claimed in Claim 2, wherein the amine- or amide-epichlorohydrin resin has one or more functional groups that contain epoxide groups or derivatives thereof.
- 5 7. Composition as claimed in any one of Claims 1 to 6, wherein the anionic polymer comprises carboxylate and/or sulphonate groups.
8. Composition as claimed in any one of Claims 1 to 6  
10 which is a detergent composition further comprising at least one surfactant.
9. Composition as claimed in Claim 7 which is a laundry rinse composition.
- 15 10. Composition as claimed in Claim 9 which comprises a fabric conditioning and/or softening compound.
11. Composition as claimed in Claim 9 which further  
20 comprises a silicone component.
12. Composition as claimed in Claim 11, wherein the ratio of amine- or amide-epichlorohydrin resin to the silicone component is from 1:1 to 30:1.
- 25 13. Composition is claimed in any one of Claims 1 to 6 which further comprises a perfume.
14. A method of treating fabric comprising applying to the  
30 fabric a fabric care composition of any one of Claims 1 to 13 as part of a laundering process.

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15. A method as claimed in Claim 14, wherein the composition is applied to the fabric during the rinse cycle.
- 5 16. A method as claimed in Claim 14, wherein the fabric comprises cellulosic fibres.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 00/09589

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C11D3/37			
According to International Patent Classification (IPC) or to both national classification and IPC			
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C11D C08G			
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched			
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) WPI Data, EPO-Internal, PAJ			
C. DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	
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X	GB 2 185 499 A (BIP CHEMICALS LTD) 22 July 1987 (1987-07-22) claims	1-3,6,7	
A	WO 98 29530 A (PROCTER & GAMBLE) 9 July 1998 (1998-07-09) cited in the application page 12, paragraph 4 -page 13, paragraph 2; claim 1 ---	1,2,4-6, 8-10, 13-16	
A	WO 98 17764 A (BASF AG) 30 April 1998 (1998-04-30) cited in the application claims 1-3,7 ---	1,2,6,8, 13,14,16	
	-/-		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.		<input checked="" type="checkbox"/> Patent family members are listed in annex.	
* Special categories of cited documents : *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed			
*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art *S* document member of the same patent family			
Date of the actual completion of the international search		Date of mailing of the international search report	
12 January 2001		19/01/2001	
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer  Saunders, T	

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Intell. Int'l Application No.  
PCT/EP 00/09589

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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